Evaluation and Comparison of Kinetic Tests Performed with the Humidity Cell, Column and Funnel Methods and Proposition of a Model with the Disposition Way

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Abstract

With the growing importance recognition of acid mine drainage evaluation, the prediction studies are becoming more frequent and more important. There are scientific consensus methods and interpretation of static test results, however, there are still doubts in the indication and interpretation of kinetic assays.

In this study, were assessed three samples with different potential acid drainage, using the kinetic three methodologies the most recognized and used in all regions of the world, being the Humidity Cell (ASTM D5744-B,) Column test (EPA 1627/2011) and Funnel test (AMIRA, 2002) during a 20-week cycle. The tests were conducted simultaneously and under controlled conditions, exactly as required by the methodology. Static tests were carried out in the ANC and NAG. Petrography analysis was done and assessed the parameters pH, alkalinity, and sulphate in the leachate.

The final results demonstrated that the same samples submitted to different methods of kinetic tests result in different amounts of cations, pH and Alkalinity in the leachate. The variations in results were mainly related to the amount of interstitial water in each method, which influenced on the solubility of species with neutralizing power.

These results are important and fundamental for the choice of which kinetic test should be performed, in prediction studies or remediation programs. With the correct choice of the most appropriate test for each type of use, we will have a higher quality of results and savings for businesses.

Keywords: ARD Prediction, kinetic assays, metal leaching.

Introduction

Acid mine drainage is the name given to the process resulting from the oxidation of sulfide compounds from the mining process. Sulfide compounds when exposed to the weather in the form of tailings, dam or any other forms of exposure, can suffer an oxidation and result in the generation of an acid effluent, mainly with a high content of sulphate. The low pH of the effluent from the acid mine drainage increase the dissolution of metals, causing significant environmental damage when released in water bodies without proper treatment.

Acid drainage is one of the major environmental problem of mining and due to the complexity of the factors to which the process of acid mine drainage is related, the process of treatment is usually expensive and long-term. Thus, is necessary that the acid drainage generation potential of a disposal material been known prior to the implementation of the operational activities.

In Brazil, the disposal of mining waste is regulated by ABNT 13029 (2017), which features on the guidelines for elaboration and presentation of the mining waste disposal project design. In this standard, evaluation is required of the potential acid drainage and neutral leaching of tailings, however, there is no a standard that regulates which tests must be performed to attend this requirement.

Among the various stages of ARD prediction, there are tests performed in laboratories. These tests to assess the acid drainage potential are divided into 2 groups: Kinetic and static.

The static tests are essay where are evaluated the potential for acid generation and neutralization. One of the first classic method for this evaluation and worldwide used is the Sobek method (1978) Acid-Base Accounting (ABA) that was later modified by Lapakko (2002) (MABA). Another test used is the NAG (Net acid Generation) proposed by Stewart (2003). This method presents the balance between the acid production and acid consumption of the mine solidwaste. Besides the balance between the acid-base production, others considerations are important, as the DRX and SEM analysis to give support to the data interpretation.

Kinetic tests are essay conducted usually in columns or funnel where a quantity of sample (some kilograms) are exposed to wet and dry cycles. The effluent leached of these extracts are usually collected and analyzed for pH, EC, Sulphate, Alkalinity and metals content. Among the various kinetic tests available in the literature, the most used are the humidity cell tests (ASTM D5744), column test (EPA 1627/2011) and funnel test (AMIRA, 2002). Although of this three kinetic test, have the same principle, some specifics procedures can result in a data with large variance.

Thus, considering the variety of testing methods for evaluation of acid drainage potential available, as well as seeking to provide subsidies to a standardization of kinetic assays in Brazil, this study aimed to evaluate the results of three samples with different acid generation potential submitted to different kinetic tests and to compare the results obtained.

Methods

Three samples were selected from mining sites with different acid drainage generation potential, using the NAPP criterion: A low potential to acid generation (NAF), the second with acid generation potential uncertain (UAF) and a third with high acid generation potential (HAF). The samples were collected in the State of Minas Gerais-Brazil, in a region of a gold mine. Was collected a total of 100 kg. The samples were crushed to 6 mm for the kinetic and ground tests for static tests.

Were prepared three columns of each type of material (NAF, UAF and HAF) for each one of the three evaluation methods: Humidity Cell (ASTM D5744-B), column test (EPA 1627/2011) and funnel test (AMIRA, 2002), as shown in Figure 1.

The procedures were performed exactly as described in the methods listed and details below:

Humidity Cell – ASTM D5744-B: This test requires that temperature and relative humidity be maintained within a constant range

a

b

Figure 1 *Picture of the three Kinetic test: a (column), b (humidity cell) and c (funnel)*

by storing the cells in an environmentally and controlled enclosure during the 6 days following the weekly 500- or 1000-mL leach. After this period, a new leaching cycle is started.

Column test – EPA 1627: This test is carried out using 2-inch columns with material less than 6 mm. Once the column has been drained after initial procedures, the humidified gas mixture with 10% of CO_2 at a rate of 1 L/min is introduced continuously through the gas at the bottom of the column. The column is allowed to sit for a period of 6 days during the humidified air cycle. This cycle is repeated after each saturation cycle. After each humidified air cycle, reagent water is introduced at the bottom of the column and after a 1 day of contact time, the leach is collected.

Funnel test – Amira (2002): This test consists in expose the crushed sample in a funnel and hold weekly cycles of addition of reagent water. Heat lamps are installed to ensure that the columns dry-out between watering. The leached are collected weekly.

For all leached, after each completed cycle, leachate collected volume was recorded. The pH was measured with Hanna HI 221-pH meter that was calibrated against commercial buffer solutions (pH 4, pH 7 and pH 10) and electrical conductivity using a conductivity meter. Leachate was filtered through a filter paper cellulose nitrate of 0.45 µm. Samples were collected and acidified with nitric acid for ICP-OES (Agilent, 5100) analysis of Al, as, Ca, Cu, Fe, Mg, Pb, and Zn. Sulphate concentrations were determined by ion Chromatography (Metrohm IC-801). The environmental conditions in the lab were kept at 20 ± 1° C.

Results and discussion

Static Tests

The selected samples were analyzed in order to verify the acid drainage generation potential using static tests. The results are presented in Table 1.

As it can be seen on table 1, the results of the static testing have indicated that the sample NAF have not presented an acid drainage generation potential, since the value of the NPP was at 156.9 kg $CaCO_3$/t, as well as the NAG value presented was <1 kg H_2SO_4 and NAG pH of 4.6, due to the high presence of carbonates in the sample. Moreover, the UAF sample has presented an uncertain potential acid drainage generation, given that the NPP was -1.2 $CaCO_3$/t and the NAG in 16.5 H_2SO_4/t and a NAGpH of 4.3. The sample HAF has already presented an acid drainage generation potential, once the value of NPP was -63.1 $CaCO_3$/t and NAG of 44.8 H_2SO_4/t and a NAG pH of 3.1.

Furthermore, it was carried out a petrographic analysis was carried aiming at evaluating the different stages of sulfides present in each sample. The results are shown in Figure 2.

The results of petrographic analyses can be seen on Figure 2 and they corroborate the static tests that had been done, once in the sample NAF was found carbonate, just as pyrite was found in the sample HAF, conversely it was found a fraction of chalcopyrite in the UAF sample. The analysis of the results of the static testing endorse the sample selection, once it has shown different acid drainage generation potential.

Each sample underwent 3 diffferent tests, that were replicated 3 times. The statistical analysis had a confidence level of 95%.

Kinetic Tests

The results of the kinetic tests are shown in the tables 2 and 3 and Figure 3.

The final pH values (week 20) are presented on table 2 covering all three samples (NAF, UAF and HAF) and the three methods evaluated (Funnel test, Humidity cell and Column test).

Regarding the NAF sample, the three methods of kinetic tests have assessed that

***Table 1** The results of the static tests*

Sample	pH 1:1	PA	PN	NPP	NAG	NAG pH
	Kg $CaCO_3$/t	Kg $CaCO_3$/t	Kg $CaCO_3$/t	Kg H_2SO_4/t	Kg H_2SO_4/t	Kg H_2SO_4/t
NAF	8.22	28.4	185.3	156,9	<1	4.6
UAF	6.37	18.4	17.2	- 1.2	16.5	4.3
HAF	5.16	93.7	30.6	- 63.1	44.8	3.1

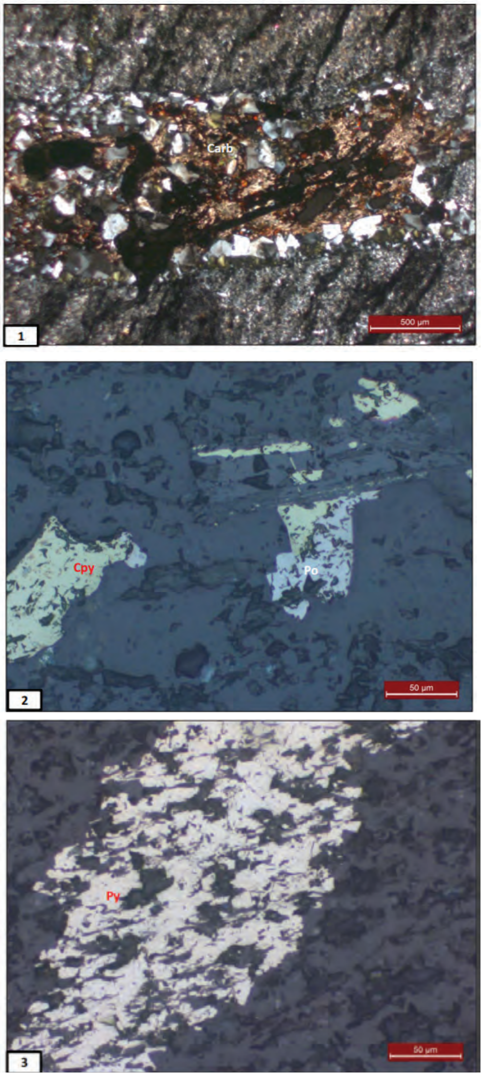


Figure 2 Petrographic analysis images: 1 (NAF), 2 (UAF), 3 (HAF)

Table 2 Final pH in the 20 weeks

	Final pH		
Samples	Funnel Test	Humidity cell	Column Test
NAF	6.91 a	6.75 a	6.89 a
UAF	6.39 a	6.67 a	6.49 a
HAF	3.38 a	6.89 b	4.62 c

there was no statistical difference in the pH value, all results are above 6, thus they endorse the static test results that indicate a sample without acid drainage generation potential during the evaluted period.

Means followed by the same letter in the lines do not differ according to t's test at 95% confidence level.

Futhermore, the UAF samples had a similar behavior, once the value of pH have not showed any statistical difference in the three methods evaluated. In fact, all pH values are above 6, what indicates that the sample UAF did not present a potential for generating acidic drainage during the period of analysis.

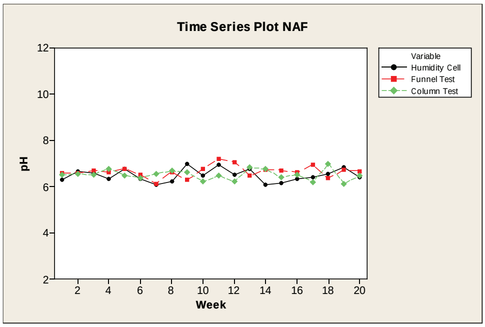
Finally, the HAF samples have shown a significant difference between the final pH concerning the three chosen methods. The Funnel test resulted in a final pH of 3.38, by the other hand , the Column Test restults show a pH of 4.62, at last the Humidity cell test presented a final pH of 6.89, thus, all of them are statistically different from each other. This result indicates that the chosen method in the kinetic test might be decisive for the assessment of potential acid drainage from a sample. The outputs show that the test of the funnel and the column test resulted in a leached with low pH, meanwhile the humidity cell test resulted in a leached with neutral pH.

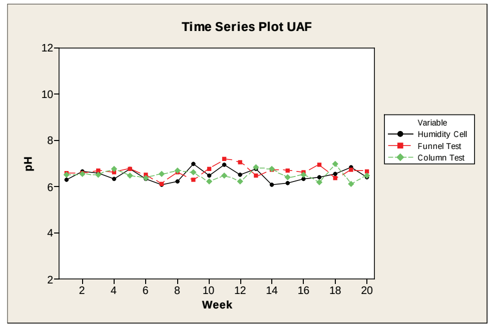
Means followed by the same letter in the lines do not differ according to t's test at 95% confidence level.

Then, Figure 3 shows pH measurement results of the leachate during the 20 weeks the experiments were performed. It can be seen that for the samples NAF and UAF there are no differences between the pH values, however, when it concerns the HAF sample, after the 10th week, the pH of the leached obtained from the Funnel Test started to decrease, which was sustained until the 13th week, therefore it stabilized in pH around 3. The same effect can be seen in the leached obtained from the

Table 3 Accumulate amount of Alkalinity and Sulphate in 20 weeks

	Alkalinity – mg $CaCO_3$			Sulphate mg SO_4		
Sample	Funnel Test	Humidity cell	Column Test	Funnel Test	Humidity cell	Column Test
NAF	163.0 a	615.0 b	656.3 b	1,879.9 d	1,323.1 e	2,472.4 f
UAF	120.8 a	219.5 b	269.6 b	809.0 d	668.1 e	1,218.5 f
HAF	58.8 a	431.2 b	270.9 c	4,429.6 d	4,329.9 d	4,377.6 d





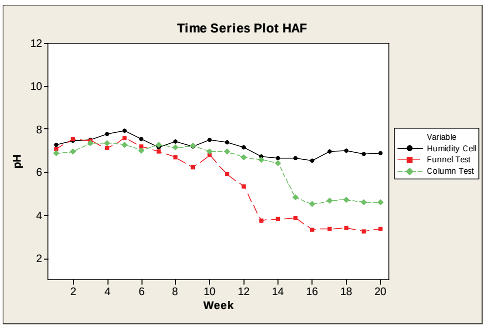


Figure 3 *Evolution of pH in the NAF, UAF e HAF samples*

Column Test, in which after the 14th week it started a trend of decrease in pH values, it stabilized the pH around 4. These results indicate that the process of weathering had different rate for each test. In order to better assess these results, it is important to determine the alkalinity and sulphate leached over the 20 weeks, as shown in table 3.

Thereby, table 3 shows that the HAF sample had a quantity of sulphate in leachate statistically equal in each of the three methods, whereas the value of alkalinity was lower concerning the funnel test, it is followed by the method of the column, the highest value of alkalinity was obtained for the leached from the test with humidity cell. It is important to point out that the amount of alkalinity in the leachate was always greater in the humidity cell and column methods, when they were compared with the method of the funnel. This result probably is related to a greater amount of interstitial water in humidity cell and Column methods, what can increase the solubility of the cations of carbonate formation, consequently, it resulted in a higher alkalinity in leachate. The impact of the increased solubilization of sulphate can be minimized because of the high solubility of these chemical species.

As a matter of fact, this observation is really relevant considering the samples that showed leaching sulfides potential and carbonates, what led to produce a self-neutralization. In this case, choosing the method of the kinetic assay can be decisive. Once the geologic formation of samples may change the solubility of some chemical species, as for example during the testing of NAF and UAF the amount of leachate sulphate was different for each of the three methods.

That way, depending on, the choice of the method used in the kinetic assay, it can reproduce the conditions of disposal of the solid waste, both in the presence or not of interstitial water, or direct exposure to sunlight, what can be a decisive factor to the process of weathering this material.

During the tests the metals concentration in the leachate have been evaluated, which will be discussed in an upcoming paper.

Conclusions

The results data have shown that the kinetic assay method can lead to different chemical results for the same sample, mostly due to the amount of surface and interstitial water and the time of contact of water and the sample, which increases the solubility of cations and consequently it can influence the leachate pH. Moreover, studies are being carried out in order to develop a mathematical model that will be able to relate the results of the different kinetic assays methods and the way of disposing solid waste, thus, the best method for each sample will be chosen.

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